

Fuel composition

5 The present invention relates to a fuel composition comprising a major amount of a specific lower alkanol-containing gasoline fuel and a minor amount of selected gasoline fuel additives.

10 Carburetors and intake systems of gasoline engines, and also injection systems for fuel metering, are contaminated to an increasing degree by impurities which are caused by dust particles from the air, uncombusted hydrocarbon residues from the combustion chamber and the crankcase vent gases conducted into the carburetor.

15 These residues shift the air-fuel ratio when idling and in the lower partial load range, so that the mixture becomes leaner, the combustion more incomplete and in turn the proportions of uncombusted or partially combusted hydrocarbons in the exhaust gas become higher and the gasoline consumption increases.

20 It is known that these disadvantages can be prevented by using fuel additives to keep valves and carburetors or injection systems of gasoline engines clean (cf., for example: M. Rossenbeck in Katalysatoren, Tenside, Mineralöladditive [Catalysts, surfactants, mineral oil additives], Eds.: J. Falbe, U. Hasserodt, p. 223, G. Thieme Verlag, Stuttgart 1978).

25 Moreover, in gasoline engines of older design, the problem of valve seat wear occurs on operation with lead-free gasoline fuels. To counteract this, valve seat wear-inhibiting additives have been developed which are based on alkali metal or alkaline earth metal compounds.

30 For trouble-free use, modern gasoline engines require fuels having a complex profile of properties which can only be ensured in combination with appropriate gasoline fuel additives. Such gasoline fuels generally consist of a complex mixture of chemical compounds and are characterized by physical quantities. However, the interplay between gasoline fuels and appropriate additives is still in need of improvement in the known fuel compositions with regard to the action of cleaning and keeping clean, and
35 the valve seat wear-inhibiting action.

It is an object of the present invention to find a more effective gasoline fuel-gasoline fuel additive composition. In particular, the intention is to find more effective additive formulations.

We have found that this object is achieved by a fuel composition which comprises a major amount of a gasoline fuel having a maximum sulfur content of 150 ppm by weight and a minor amount of at least one gasoline fuel additive having detergent action or having a valve seat wear-inhibiting action, wherein this gasoline fuel additive has at least one hydrophobic hydrocarbon radical having a number-average molecular weight (MN) of from 85 to 20 000 and at least one polar moiety, and wherein the fuel composition also has a content of at least one lower alkanol of from about 5 to 75% by volume.

10 The polar moiety is selected from:

(a) mono- or polyamino groups having up to 6 nitrogen atoms, of which at least one nitrogen atom has basic properties,

15 (b) nitro groups, if appropriate in combination with hydroxyl groups,

(c) hydroxyl groups in combination with mono- or polyamino groups, in which at least one nitrogen atom has basic properties,

20 (d) carboxyl groups or their alkali metal or their alkaline earth metal salts,

(e) sulfonic acid groups or their alkali metal or alkaline earth metal salts,

25 (f) polyoxy-C2- to -C4-alkylene groups which are terminated by hydroxyl groups, mono- or polyamino groups, in which at least one nitrogen atom has basic properties, or by carbamate groups,

(g) carboxylic ester groups,

30 (h) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amino and/or imido groups and

(i) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

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The alkanol used in accordance with the invention is preferably a straight-chain or branched, saturated C₁-C₆-mono- or -diol, in particular a C₁-C₃-mono alkanol, such as methanol, ethanol, n- or i-propanol, or a mixture of a plurality of these alkanols.

The alkanol content, based on the total volume of the fuel composition, is a maximum of 75% by volume, for example from 5 to 75% by volume, preferably from 10 to 65% by volume, in particular from 20 to 55% by volume, for example 30 – 40% by volume or 40 – 50% by volume.

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The content of further alcohols and ethers in the gasoline fuel is normally relatively low. Typical maximum contents are 7% by volume for tert-butanol, 10% by volume for isobutanol and 15% by volume for ethers having 5 or more carbon atoms in the molecule.

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The maximum aromatics content of the gasoline fuel is preferably 40% by volume, in particular 38% by volume. Preferred ranges for the aromatics content are from 20 to 42% by volume, in particular from 25 to 40% by volume.

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The maximum sulfur content of the gasoline fuel is preferably 100 ppm by weight, in particular 50 ppm by weight. Preferred ranges for the sulfur content are from 0.5 to 150 ppm by weight, in particular from 1 to 100 ppm by weight.

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In a preferred embodiment, the gasoline fuel has a maximum olefin content of 21% by volume, preferably 18% by volume, in particular 10% by volume. Preferred ranges for the olefin content are from 6 to 21% by volume, in particular from 7 to 18% by volume.

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In a further preferred embodiment, the gasoline fuel has a maximum benzene content of 1.0% by volume, in particular 0.9% by volume. Preferred ranges for the benzene content are from 0.5 to 1.0% by volume, in particular from 0.6 to 0.9% by volume.

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In a further preferred embodiment, the oxygen content of the gasoline fuel is a maximum of 2.7% by weight, and is preferably from 0.1 to 2.7% by weight, in particular from 1.0 to 2.7% by weight, especially from 1.2 to 2.0% by weight.

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Particular preference is given to a gasoline fuel which at the same time has a maximum aromatics content of 38% by volume, a maximum olefin content of 21% by volume, a maximum sulfur content of 50 ppm by weight, a maximum benzene content of 1.0% by volume and an oxygen content of from 1.0 to 2.7% by weight.

The above percentages by volume for all of them, benzene, aromatics and oxygen content are each based on the volume of the mineral gasoline fuel component, i.e. without additives and without alkanol.

The summer vapor pressure of the gasoline fuel is typically a maximum of 70 kPa, in particular 60 kPa (each at 370C).

5 The research octane number ("RON") of the gasoline fuel is generally from 90 to 100. A typical range for the corresponding motor octane number ("MON") is from 80 to 90.

The specifications mentioned are determined by customary methods (DIN EN 228).

10 The hydrophobic hydrocarbon radical in the gasoline fuel additives, which ensures sufficient solubility in the fuel, has a number-average molecular weight (Mn) of from 85 to 20 000, especially from 113 to 10 000, in particular from 300 to 5 000. Typical hydrophobic hydrocarbon radicals which can be used, in particular in conjunction with the polar moieties (a), (c), (h) and (i) are the polypropenyl, polybutenyl and polyisobutenyl radical each having Mn = from 300 to 5 000, especially from 500 to
15 2 500, in particular from 750 to 2 250.

Individual gasoline fuel additives having detergent action or having valve seat wear-inhibiting action include the following:

20 Additives comprising mono- or polyamino groups (a) are preferably polyalkenemono- or polyalkenepolyamines based on polypropene or on highly reactive (i.e. having predominantly terminal double bonds, usually in the alpha- and beta-position) or conventional (i.e. having predominantly internal double bonds) polybutene or polyisobutene having Mn = from 300 to 5000. Such additives based on highly reactive
25 polyisobutene, which can be prepared from the polyisobutene which may comprise up to 20% by weight of n-butene units by hydroformylation and reductive amination with ammonia, monoamines or polyamines, such as dimethylaminopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine, are disclosed in particular in EP-A 244 616. When polybutene or polyisobutene having
30 predominantly internal double bonds (usually in the beta and gamma position) are used as starting materials in the preparation of the additives, a possible preparative route is by chlorination and subsequent amination or by oxidation of the double bond with air or ozone to give the carbonyl or carboxyl compound and subsequent amination under reductive (hydrogenating) conditions. The amines used here for the amination may be
35 the same as those used above for the reductive amination of the hydroformylated highly reactive polyisobutene. Corresponding additives based on polypropene are described in particular in WO-A 94/24231.

40 Further preferred additives containing monoamino groups (a) are the hydrogenation products of the reaction products of polyisobutenes having an average degree of

polymerization P = from 5 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO-A 97/03946.

Further preferred additives comprising monoamino groups (a) are the compounds obtainable from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino alcohols, as described in particular in DE-A 196 20 262.

Additives comprising nitro groups, if appropriate in combination with hydroxyl groups, (b) are preferably reaction products of polyisobutenes having an average degree of polymerization P = from 5 to 100 or from 10 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO-A 96/03367 and WO-A 96/03479. These reaction products are generally mixtures of pure nitropolyisobutanes (e.g. alpha, beta-dinitropolyisobutane) and mixed hydroxynitropolyisobutanes (e.g. alpha-nitro-beta-hydroxypolyisobutane).

Additives comprising hydroxyl groups in combination with mono- or polyamino groups (c) are in particular reaction products of polyisobutene epoxides obtainable from polyisobutene having preferably predominantly terminal double bonds and Mn from 300 to 5 000, with ammonia or mono- or polyamines, as described in particular in EP-A 476 485.

Additives comprising carboxyl groups or their alkali metal or alkaline earth metal salts (d) are preferably copolymers of C₂-C₄₀-olefins with maleic anhydride which have a total molar mass of from 500 to 20 000 and of whose carboxyl groups some or all have been converted to the alkali metal or alkaline earth metal salts and any remainder of the carboxyl groups has been reacted with alcohols or amines. Such additives are disclosed in particular by EP-A 307 815. Such additives serve mainly to prevent valve seat wear and can, as described in WO-A 87/01126, advantageously be used in combination with customary fuel detergents such as poly(iso)butenamines or polyetheramines.

Additives comprising sulfonic acid groups or their alkali metal or alkaline earth metal salts (e) are preferably alkali metal or alkaline earth metal salts of an alkyl sulfosuccinate, as described in particular in EP-A 639 632. Such additives serve mainly to prevent valve seat wear and can be used advantageously in combination with customary fuel detergents such as poly(iso)butenamines or polyetheramines.

Additives comprising polyoxy-C₂- to C₄-alkylene moieties (f) are preferably polyethers or polyetheramines which are obtainable by reaction of C₂- to C₆₀-alkanols, C₆- to C₃₀-

alkanediols, mono- or di-C₂-C₃₀-alkylamines, C₁-C₃₀-alkylcyclohexanols or C₁-C₃₀-alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group and, in the case of the polyetheramines, by subsequent reductive amination with ammonia, monoamines or polyamines. Such products are described in particular in EP-A 310 875, EP-A 356 725, EP-A 700 985 and US-A 4 877 416. In the case of polyethers, such products also have carrier oil properties. Typical examples of these are tridecanol butoxylates, isotridecanol butoxylates, isononylphenol butoxylates and polyisobutenol butoxylates and propoxylates and also the corresponding reaction products with ammonia.

Additives comprising carboxylic ester groups (g) are preferably esters of mono-, di- or tricarboxylic acids with long-chain alkanols or polyols, in particular those having a minimum viscosity of 2 mm²/s at 100°C, as described in particular in DE-A 38 38 918. The mono-, di- or tricarboxylic acids used may be aliphatic or aromatic acids, and particularly suitable ester alcohols or ester polyols are long-chain representatives having, for example, from 6 to 24 carbon atoms. Typical representatives of the esters are adipates, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, of isononanol, of isodecanol and of isotridecanol. Such products also have carrier oil properties.

Additives comprising moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups (h) are preferably corresponding derivatives of polyisobutenylsuccinic anhydride which are obtainable by reacting conventional or highly reactive polyisobutene having Mn = from 300 to 5 000 with maleic anhydride by a thermal route or via the chlorinated polyisobutene. Particular interest attaches to derivatives with aliphatic polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. Such gasoline fuel additives are described in particular in US-A 4 849 572.

Additives comprising moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines (i) are preferably reaction products of polyisobutene-substituted phenols with formaldehyde and mono- or polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine. The polyisobutenyl-substituted phenols may stem from conventional or highly reactive polyisobutene having Mn = from 300 to 5 000. Such "polyisobutene-Mannich bases" are described in particular in EP-A 831 141.

For a more precise definition of the gasoline fuel additives detailed individually, reference is explicitly made here to the disclosures of the abovementioned prior art documents.

The fuel composition according to the invention may additionally comprise further customary components and additives. These include primarily carrier oils without marked detergent action, for example mineral carrier oils (base oils), in particular those of the viscosity class "Solvent Neutral (SN) 500 to 2 000", and synthetic carrier oils
5 based on olefin polymers having M_n = from 400 to 1800, in particular based on polybutene or polyisobutene (hydrogenated or nonhydrogenated), on poly- α -olefins or poly(internal olefin)s.

Useful solvents or diluents (when providing additive packages) are aliphatic and
10 aromatic hydrocarbons such as Solvent Naphtha.

Further customary additives are corrosion inhibitors, for example based on ammonium salts of organic carboxylic acids, said salts tending to form films, or of heterocyclic aromatics for nonferrous metal corrosion protection, antioxidants or stabilizers, for
15 example based on amines such as p-phenylenediamine, dicyclohexylamine or derivatives thereof or of phenols such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid, demulsifiers, antistats, metallocenes such as ferrocene or methylcyclopentadienylmanganese tricarbonyl, lubricity additives such as certain fatty acids, alkenylsuccinic esters, bis(hydroxyalkyl) fatty amines, hydroxyacetamides or
20 castor oil and also markers. Amines are also optionally added to lower the pH of the fuel.

Also useful for the fuel composition according to the invention are in particular combinations of the gasoline fuel described with a mixture of gasoline fuel additives
25 having the polar moiety (f) and corrosion inhibitors and/or lubricity additives based on carboxylic acids or fatty acids which may be present as monomeric and/or dimeric species. Typical mixtures of this type comprise polyisobutanamines in combination with alkanol-started polyethers such as tridecanol or isotridecanol butoxylates or propoxylates, polyisobutenamines in combination with alkanol-started polyetheramines
30 such as tridecanol or isotridecanol butoxylate-ammonia reaction products and alkanol-started polyetheramines such as tridecanol or isotridecanol butoxylate reaction products in combination with alkanol-started polyethers such as tridecanol or isotridecanol butoxylates or propoxylates, used together with the corrosion inhibitors and/or lubricity additives mentioned.

35 The gasoline fuel additives having the polar moieties (a) to (i) mentioned, and also the other components mentioned, are metered into the gasoline fuel and exhibit their action there. The components and/or additives may be added to the fuel individually or as a concentrate prepared beforehand ("additive package").
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The gasoline fuel additives having the polar moieties (a) to (i) mentioned are added to the gasoline fuel typically in an amount of from 1 to 5 000 ppm by weight, especially from 5 to 3 000 ppm by weight, in particular from 10 to 1 000 ppm by weight. The other components and additives mentioned are, if desired, added in amounts customary for this purpose.

In the fuel composition according to the invention, it is surprisingly possible with distinctly less detergent or valve seat wear inhibitor to achieve the same action of cleaning or keeping clean, or valve seat wear-inhibiting action as for comparable fuel compositions without lower alkanol addition. Moreover, the use of the same amounts of detergent or valve seat wear inhibitor in the fuel composition according to the invention, compared to conventional fuel compositions, surprisingly results in a distinctly better action of cleaning or keeping clean, and valve seat wear-inhibiting action.

In addition, the fuel composition according to the invention additionally exhibits advantages to the effect that fewer deposits are formed in the combustion chamber of the gasoline engine and that less additive is entrained into the engine oil via the fuel dilution.

The invention further relates to

- i) the use of a lower alkanol in low-sulfur gasoline fuels to improve the action of an additive having detergent action or having valve seat wear-inhibiting action as defined above;
- ii) a process for improving the additive action of an additive having detergent action or having valve seat wear-inhibiting action as defined above in low-sulfur gasoline fuels, by admixing the gasoline fuel with an effective amount of a lower alcohol;
- iii) the use of a combination of lower alcohol and at least one additive having detergent action or having valve seat wear-inhibiting action as defined above to reduce combustion chamber deposits and/or to reduce deposits in the intake system of a gasoline engine;
- iv) the use of a combination of lower alcohol and additive having valve seat wear-inhibiting action as defined above as a valve seat wear-inhibitor for gasoline fuels.

The examples which follow are intended to illustrate the invention without restricting it.

Examples:

5 The gasoline fuel additive used was a commercial additive package comprising 60% by weight of detergent additive, polyisobutenamine ($M_n = 1\,000\text{ g/mol}$), and 32% by weight of carrier oil (tridecanol etherified with 22 units of butylene oxide).

The gasoline fuels used were those listed below with the particular specification stated, and GF 1 (parameters see Table 1) is a typical commercially available fuel.

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Table 1

Specification	GF 1
Aromatics content [% by vol.]	39.8
Paraffin content [% by vol.]	47.7
Olefin content [% by vol.]	12.5
Sulfur content [ppm by weight]	35
Density [15 °C] [kg/m^3]	743.6
Initial boiling point	34.5 °C
10 % volume	50 °C
50 % volume	85 °C
90 % volume	150.5 °C
Final boiling point	189.0 °C

- 15 GF 2 = GF 1 + 10% by vol. of EtOH
GF 3 = GF 1 + 50% by vol. of EtOH

Preparation of the fuel compositions20 **Example 1 (comparative experiment)**

150 or 200 mg of additive package were dissolved in 1 kg of GF 1 according to Table 1.

25 **Example 2 (inventive)**

Example 1 was repeated except that GF 2 was used instead of GF 1.

Example 3 (inventive)

Example 1 was repeated except that GF 3 was used instead of GF 1

5 Performance investigations**Example 4**

10 Gasoline fuels according to Examples 1 to 3 were investigated for their influence on the intake valve deposits (IVD) and on the total combustion deposits (TCD). This was effected with the aid of engine tests which were carried out in test rig experiments with a Mercedes-Benz engine M102 E according to CEC F-05-A-93. The IVD values for additized and nonadditized fuels are compiled in the following Table 2.

15 In addition, the amount of total combustion deposits (TCD) was determined in the same experimental series for each of the four cylinders of the engine. The particular average value is likewise quoted in Table 2. To determine the TCD value, the procedure was similar to the method CEC F-20-A-98.

Table 2

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Fuel	GF 1			GF 2			GF 3		
Amount of additive [mg/kg]	0	150	200	0	150	200	0	150	200
IVD ¹⁾ [mg/valve]	269	85	23	293	98	15	239	31	3
TCD ²⁾ [mg/cylinder]	1778	1864	1807	1677	1668	1713	1056	1248	764

¹⁾ Intake Valve Deposits

²⁾ Total Combustion Deposits

25 As is evident from Table 2, the admixing of relatively large amounts of ethanol (i.e. > 10%) to the gasoline fuel results in surprisingly little formation of valve or combustion chamber (cylinder) deposits being observed.